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PATENT ABSTRACTS OF JAPAN

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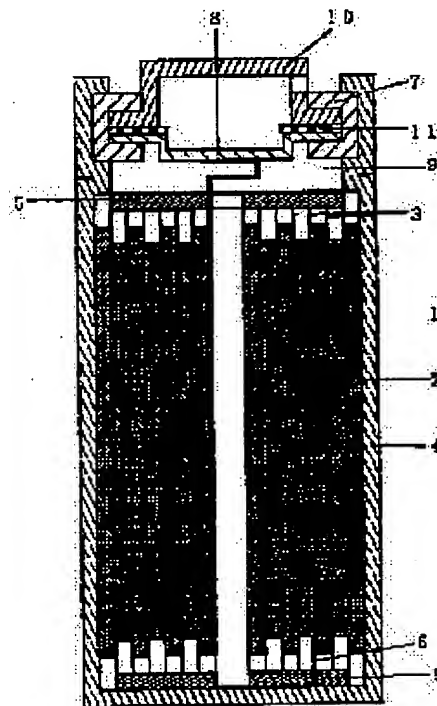
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(54) SECONDARY BATTERY

(57)Abstract:

PURPOSE: To prevent the capacity deterioration caused by charge/discharge cycles by adding and mixing one or more oxides selected among Al_2O_3 , In_2O_3 , SnO_2 , ZnO to a lithium containing composite oxide, and generating the positive electrode of a lithium ion secondary battery.

CONSTITUTION: MnO_2 and Li_2CO_3 are mixed at the atomic ratio of 1:2 between Li and Mn, and the mixture is baked in the air at 800°C for 20hrs to obtain LiMn_2O_4 , for example. Al_2O_3 is selected among Al_2O_3 , In_2O_3 , SnO_2 , and ZnO , and Al_2O_3 of 2 pts.wt. and graphite of 8 pts.wt. are added to LiMn_2O_4 , of 87 pts.wt. to obtain slurry by wet blending. The slurry is uniformly applied on both faces of an aluminum foil having the thickness of 0.02mm, for example, and serving as a positive electrode current collector, and it is pressed and molded by a roller press machine after drying to form a band-like positive electrode 2. A porous polypropylene separator 3 is sandwiched between a negative electrode 1 and the positive electrode 2, and they are wound into a roll shape into a wound body to obtain a battery element. The capacity deterioration caused by charge/discharge cycles can be prevented.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a performance improvement of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] While miniaturization of electronic equipment and lightweight-ization are advanced, the request of the rechargeable battery of a high-energy density has become strong further as the power. In order to reply to the request, the nonaqueous electrolyte rechargeable battery attracted attention and the utilization has been tried. although the so-called lithium secondary battery which uses a lithium metal especially for a negative electrode was regarded as possibility being the largest, in order that the performance deteriorates remarkably, and a metal lithium negative electrode may be powder-ized by the repeat of charge and discharge, and a metal lithium may separate it to a dendrite and it may cause internal short-circuit, a problem is in a practical cycle life and it is now -- utilization is difficult Then, the nonaqueous electrolyte rechargeable battery which uses the carbon electrode using receipts and payments of the lithium ion to carbon as a negative electrode is under development recently. At present, this cell is named a lithium ion rechargeable battery, will be begun in 1990, was introduced to the world by this invention person etc., it is recognized so that it is called rechargeable battery "a lithium ion rechargeable battery" of the next generation also in the cell industry and a society (magazine Progress In Batteries & SolarCells, Vol. 9, 1990p209), and it has required the spur for the utilization. Lithium inclusion multiple oxides (for example, LiMn_2O_4 , LiCoO_2 , LiNiO_2 , etc.) are typically used for a positive-electrode material, and carbonaceous materials, such as corks and graphite, are used for a negative electrode. Actually, LiCoO_2 is used for a positive electrode, a special carbon material (pseudo-graphite material with a certain amount of random layer structure) is used for a negative electrode, and little practical use of the lithium ion rechargeable battery with the energy density of about 200Whs/l. has already been carried out. The energy density of the existing nickel-cadmium battery is 100-150Whs/l., and, as for the energy density of a lithium ion rechargeable battery, exceeds it of the existing cell far. However, as a big fault, it is that a material cost is quite high first. In considering a cheap lithium ion rechargeable battery, since [like resources], a price fall of cobalt cannot be desired in the future. However, lithium manganese multiple oxides (LiMn_2O_4 , LiMnO_2 , etc.) are very attractive at the point of a cheap material. Another fault is that a degradation of the capacity accompanied by a charge-and-discharge cycle is [a lithium ion rechargeable battery] large. And the degradation is remarkably large what used the lithium manganese multiple oxide as a positive-electrode material. As for a carbon negative electrode, by electric discharge, the ** dope of the carbon to the lithium ion is only carried out by doping lithium ion in charge to the carbon in an electrode, the charge-and-discharge property extremely stabilized since carbon itself was not accompanied by change of the big crystal structure in case of charge and discharge is shown, there are few property degradations accompanied by charge and discharge, and the repeat of 1000 times or more of charges and discharges is specifically also possible. However, a degradation of the capacity accompanied by the cycle of an actual lithium ion rechargeable battery is governed by property degradation of a positive electrode, and cannot be called sufficiently satisfactory level.

[0003]

[Problem(s) to be Solved by the Invention] this invention relates to an improvement of the cycle property of the nonaqueous electrolyte rechargeable battery which makes a lithium inclusion multiple oxide a main positive-active-material material.

[0004]

[Means for Solving the Problem] The means of a technical-problem resolution comes to add one or more sorts of oxides which mix with the lithium inclusion multiple oxide which is a positive active material, and are chosen out of aluminum 2O_3 , In_2O_3 , and SnO_2 and ZnO all over a positive electrode.

[0005]

[Function] If lithium inclusion multiple oxides (LiMn_2O_4 , LiMnO_2 , LiCoO_2 , LiNiO_2 , etc.) are used for a positive electrode, in the state of charge, lithium ion will be in the status that the ** dope was carried out, and any multiple oxide will become unstable. Therefore, since a positive active material changes gradually and loses the charge-and-discharge function while repeating charge and discharge repeatedly, capacity deteriorates in connection with the cycle. Then, this invention person used to find out that the capacity degradation accompanied by the increase of the stability of the positive active material of the charge status and a charge-and-discharge cycle serves as a parvus nonaqueous electrolyte rechargeable battery extremely by

mixing with active material one or more sorts of oxides chosen out of aluminum₂O₃, In₂O₃, and SnO₂ and ZnO, and adding all over a positive electrode, as a result of inquiring zealously for the purpose of stabilization of the positive active material in the charge status.

[0006]

[Example] Hereafter, an example explains this invention still in detail.

[0007] this invention is explained about a concrete cylinder type cell, referring to example 1 view 1. Drawing 1 shows the whole cell structure of this example. The cell element which is a power generation element for carrying out this invention was prepared as follows. The polyvinylidene-fluoride (PVDF) 10 weight section was added to 90 weight section of the meso carbon micro bead (d002=3.37**) which heat-treated at 2800 degrees C as a binder, wet blending was carried out to the N-methyl-2-pyrrolidone which is a solvent, and it was made the slurry (the shape of a paste). And this slurry was uniformly applied to both sides of copper foil with a thickness [used as the current collection field] of 0.01mm, pressurization molding was carried out with the roller-press machine after xeransis, and the beltlike negative electrode (1) was created. Then, the positive electrode was prepared as follows. Commercial manganese dioxide (MnO₂) and the lithium carbonate (Li₂CO₃) were mixed so that the atomic ratio of Li and Mn might turn into the composition ratio of 1:2, this was calcinated at 800 degrees C among air for 20 hours, and LiMn₂O₄ was adjusted. The aluminum₂O₃ 2 weight section and the graphite 8 weight section may be added to 87 weight section of this LiMn₂O₄, it mixes, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene-fluoride 3 weight section and a solvent as a binder further is added and carried out, and it is made a slurry (the shape of a paste). This slurry was uniformly applied to both sides of an aluminum foil with a thickness [used as the positive-electrode current collection field] of 0.02mm, pressurization molding was carried out with the roller-press machine after xeransis, and the beltlike positive electrode (2) was created. In this way, the negative electrode (1) and positive electrode (2) which were created were wound up in the shape of a roll in the meantime on both sides of the separator (3) made from porous material polypropylene, and created the cell element as winding field with a mean outer diameter of 15.7mm. Next, an electric insulating plate (5) is installed in the pars basilaris ossis occipitalis of an iron cell can (4) which performed nickel plating, and the above-mentioned cell element is contained. The negative-electrode lead (6) taken out from the cell element is welded to the base of the above-mentioned cell can, and the mixed solution of the ethylene carbonate (EC) and diethyl carbonate (DEC) which melted one mol [l.] LiPF₆ into the cell can is poured in as electrolytic solution. Then, an electric insulating plate (5) is installed also in the upper part of a cell element, a gasket (7) is inserted in, and an explosion-proof valve (8) is installed in the interior of a cell, as shown in drawing 1. The positive-electrode lead (9) taken out from the cell element is welded before injecting the electrolytic solution into this explosion-proof valve. On the explosion-proof valve, the lock out lid (10) used as a positive-electrode external terminal was piled up on both sides of the doughnut type PTC switch (11), and the cell (A) with an outer diameter [of 16.5mm] and a height of 65mm was completed with the cell structure which shows the edge of a cell can in drawing 1 in total.

[0008] The positive electrode which carries out example use of a comparison was created by the conventional method, and all others were made the same as that of an example 1, and created the cell (X) by the conventional method. The positive electrode by the conventional method is prepared as follows. 8 weight section mixture of the graphite is carried out, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene-fluoride 3 weight section and a solvent as a binder further is added and carried out to 89 weight section of powdered LiMn₂O₄ adjusted in the example 1, and it is made a slurry (the shape of a paste). This slurry was uniformly applied to both sides of an aluminum foil with a thickness [used as the positive-electrode current collection field] of 0.02mm, pressurization molding was carried out with the roller-press machine after xeransis, and the beltlike positive electrode (2c) was created. The rest wound up the same negative electrode (1) as what was created in this positive electrode (2c) and example 1 in the shape of a roll in the meantime on both sides of the separator (3) made from porous material polypropylene, created the cell element with a mean outer diameter of 15.7mm, completely, after that, was made the same as that of an example 1, and created the cell (X).

[0009] SnO₂ 2 weight section and the graphite 8 weight section are mixed among 87 weight section of adjusting-in example 2 example 1 LiMn₂O₄, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene-fluoride 3 weight section and a solvent as a binder further is added and carried out, and it is made a slurry (the shape of a paste). Then, it acted to both sides of an aluminum foil with a thickness [used as the positive-electrode current collection field] of 0.02mm as ** City of this slurry uniformly, pressurization molding was carried out with the roller-press machine after xeransis, and the beltlike positive electrode (2b) was created. The rest wound up the same negative electrode (1) as what was created in this positive electrode (2b) and example 1 in the shape of a roll in the meantime on both sides of the separator (3) made from porous material polypropylene, created the cell element with a mean outer diameter of 15.7mm, completely, also after that, was made the same as that of an example 1, and created the cell (B).

[0010] a test result -- after each cell created in the examples 1 and 2 and the example of a comparison in this way made the aging term of 12 hours pass in ordinary temperature for the purpose of the stabilization inside a cell, it set the charge upper limit voltage as 4.2V, performed charge of 8 hours in ordinary temperature, similarly performed electric discharge to termination voltage 3.0V by 800mA constant-current discharge about all cells in ordinary temperature, and calculated the initial electric-discharge capacity of each cell Each cell performed the charge-and-discharge cycle examination in the 40-degree C thermostat after that. The charging current was 400mA, the charge upper limit voltage was set as 4.2V, charge of 4 hours was performed, electric discharge was performed to termination voltage 3.0V in 800mA constant-current discharge, charge and discharge were repeated, and the electric discharge capacity in 800mA electric discharge of each cell in

40 cycle and 100 cycle time was calculated. The result is as having collected into Table 1. Even if the cell (A) by this invention and (B) repeat charge and discharge, they have few the capacity falls, and the capacity difference with the cell (X) by the conventional technique becomes quite large at each [which are 40 cycle and 100 cycle] time as shown in Table 1. Like the lithium ion battery created by this example, when using a lithium manganese multiple oxide (LiMn_2O_4) for a positive active material, with the conventional technique, capacity becomes less quite abruptly in the charge-and-discharge cycle in the elevated-temperature status especially so that a cell (X) may see. At the 100 cycle time, it will already become the capacity like the half of initial capacity.

表 1

| | 初期容量 mA h | 40サイクル時点の容量 mA h | 100サイクル時点での容量 mA h |
|--------|--------------|---------------------|-----------------------|
| 電池 [A] | 970 | 912 | 881 |
| 電池 [B] | 950 | 893 | 874 |
| 電池 [X] | 980 | 782 | 520 |

However, as shown in Table 1, also in the cell which used the lithium manganese multiple oxide (LiMn_2O_4) for the positive electrode as a positive active material by the cell (A) by this invention which carried out addition mixture of aluminum 2O_3 and SnO_2 , and (B), extremely, a degradation degree decreases and the electric discharge capacity of 870-880mAh is obtained also at the 100 cycle time. This also exceeds the initial energy density of the lithium ion rechargeable battery which used the cobalt which is about 230Whs/l. if it is made an energy density, and is commercialized now. Moreover, in internal resistance change, it is at the 100 cycle end time, and it was checked to change of some dozens milli ohms being seen by the cell (X) by the conventional method that internal resistance change of the cell by this invention has very little (A) and (B) at a number milli ohm. this invention can improve sharply the capacity degradation accompanied by the cycle which was the biggest fault of a lithium ion rechargeable battery as mentioned above. In addition, although the above-mentioned example explained the case where the effect of this invention used LiMn_2O_4 as a positive active material as an example which appears most notably, also in the nonaqueous electrolyte rechargeable battery which uses other lithium inclusion multiple oxides, such as LiCoO_2 and LiNiO_2 , as a positive active material, this invention expresses the improvement effect. Moreover, although the above-mentioned example explained the case where mixed to the positive active material, added aluminum 2O_3 and SnO_2 , and a positive electrode was created, In_2O_3 and ZnO show the same addition effect.

[0011]

[Effect of the Invention] The capacity degradation accompanied by the charge-and-discharge cycle which is the old big fault of a lithium ion rechargeable battery by carrying out addition mixture of one or more sorts of oxides which were described above, and which are chosen as lithium inclusion multiple oxides (for example, LiMn_2O_4 , LiCoO_2 , LiNiO_2 , etc.) out of aluminum 2O_3 , In_2O_3 , and SnO_2 and ZnO if it is in this invention like, and creating the positive electrode of a lithium ion rechargeable battery is sharply improvable. Especially, it is the high capacity and the longevity life which the improvement effect is remarkable in the lithium ion rechargeable battery using a lithium manganese multiple oxide as a positive active material, and can fully be replaced with the existing rechargeable battery, and a cheap lithium ion rechargeable battery can be offered now, and the industrial value is size.

[Translation done.]